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TECHNICAL REPORT DATA

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1 REPORT NO	2	3 RECIPIENT'S ACCESSION NO
4 TITLE AND SUBTITLE Carbon Disulfide, Carbonyl Sulfide: Literature Review and Environmental Assessment		5 REPORT DATE January 1976 6 PERFORMING ORGANIZATION CODE
7 AUTHOR(S) Thomas O. Peyton, Robert V. Steele, and William R. Mabey		8 PERFORMING ORGANIZATION REPORT NO
9 PERFORMING ORGANIZATION NAME AND ADDRESS Stanford Research Institute Menlo Park, California 94025		10 PROGRAM ELEMENT NO 11 CONTRACT/GRANT NO 68-01-2940, Task 023.
12 SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency 401 M. Street, S.W. Washington, D.C. 20460		13 TYPE OF REPORT AND PERIOD COVERED Final 14 SPONSORING AGENCY CODE

15 SUPPLEMENTARY NOTES

16 ABSTRACT

Carbon disulfide (CS_2) and carbonyl sulfide (COS) are volatile substances of moderate toxicity, odor, and environmental lifetimes (days). Vapors emitted from sources are expected to follow normal atmospheric dispersion principles. Each compound is produced from anthropogenic as well as natural sources. The most significant anthropogenic emission for CS_2 is from commercial usages where the atmosphere serves as the natural sink. The use of nonselective reducing catalysts may emit significant quantities of COS. Little is known of the toxic thresholds for COS; however, the significant industrial usage of CS_2 has provided appreciable industrial hygiene records on effects. Based on industrial effects records, and until better data on chronic exposures become available, we tentatively recommend that limiting long-term averaged concentrations to 300 $\mu g/m^3$ CS_2 should be sufficient for protection against adverse health effects. By chemical and biological analogy to CS_2, the corresponding level for COS would be 600 $\mu g/m^3$.

17 KEY WORDS AND DOCUMENT ANALYSIS

a DESCRIPTORS	b IDENTIFIERS/OPEN ENDED TERMS	c COSATI Field/Group
Ecology	Carbon Disulfide	6F
Organic Compound	Carbonyl Sulfide	7C
Assessments	CS_2	10A
Criteria	COS	
Standards	Energy systems	

18 DISTRIBUTION STATEMENT	19 SECURITY CLASS (This Report)	21 NO OF PAGES
Document is available to the public through the National Technical Information Services Springfield, VA 22151	20 SECURITY CLASS (This page)	61 22 PRICE

EPA Form 2220-1 (9-73)

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STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 U.S.A.

Final Report

January 1976

CARBON DISULFIDE, CARBONYL SULFIDE

Literature Review and Environmental Assessment

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WASHINGTON D.C. 20460

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I INTRODUCTION

This report, prepared for the Environmental Protection Agency under Contract No. 68-01-2940, Task 023, is subsidiary to the primary task of ranking ten hazardous substances/agents for the EPA by the STAR Ranking Objective Subsystem. The purpose of this supplemental report is to provide information that will allow the EPA to know the tolerable concentrations of carbon disulfide and carbonyl sulfide in the ambient air.

II SUMMARY

Carbon disulfide (CS_2) and carbonyl sulfide (COS) are volatile substances of moderate toxicity, odor, and environmental lifetimes (days). Vapors emitted from sources are expected to follow normal atmospheric dispersion principles. Each compound is produced from anthropogenic as well as natural sources. The most significant anthropogenic emission for CS_2 is from commercial usages where the atmosphere serves as the natural sink. The use of nonselective reducing catalysts may emit significant quantities of COS. Little is known of the toxic thresholds for COS; however, the significant industrial usage of CS_2 has provided appreciable industrial hygiene records on effects. Based on industrial effects records, and until better data on chronic exposures become available, we tentatively recommend that limiting long-term averaged concentrations to 100 $\mu g/m^3$ CS_2 should be sufficient for protection against adverse health effects. By chemical and biological analogy to CS_2, the corresponding level for COS would be 400 $\mu g/m^3$.

III LITERATURE REVIEW AND ASSESSMENT

Chemical and Physical Properties

General Characteristics

Carbon Disulfide

Carbon disulfide (CS_2) is a colorless volatile liquid of moderate solubility in water with a partition coefficient of about 100 (octanol/water) (CRC, 1971;* Leo et al., 1971*). Using the rate of evaporation approximation and assigned parameters as developed by Mackay and Wolkoff (1973),† the half-life for evaporation from a saturated water solution is 11 minutes. Some of the physical and chemical properties of CS_2 are given in Table 1.

Table 1

PHYSICAL AND CHEMICAL PROPERTIES OF CS_2

Molecular weight:	76.13
Specific gravity:	1.26 (20 C)
Melting point:	-108.6 C
Boiling point:	46.3 C
Vapor density:	2.63 (air = 1)
Vapor pressure:	360 mm Hg (25 C)
Solubility:	2.2 g/liter of water
1 mg/m^3 = 0.32 ppm	
1 ppm = 3.12 mg/m^3	

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*CRC (1971). Handbook of Chemistry and Physics (Chemical Rubber Company, Cleveland, Ohio).

*Leo, A., C. Hansch, and D. Elkins (1971). "Partition Coefficients and Their Uses." Chem. Rev., Vol. 71, No. 6.

†Mackay, D., and A. W. Wolkoff (1973). "Rate of Evaporation of Low Solubility Contaminants from Water Bodies to Atmosphere." Environ. Sci. Tech., Vol. 7, p. 611.

CS_2 is a linear molecule and has the structural representation

$$S = C = S \quad . \qquad (1)$$

Carbonyl Sulfide

Carbonyl sulfide (COS) is a colorless flammable gas of moderate solubility in water. It is 16 times more soluble in alcohol and 90 times more soluble in toluene than in water (Patty, 1963).* The chemistry of COS has been reviewed by Fern (1957).* Some of the physical and chemical properties of COS are given in Table 2.

Table 2

PHYSICAL AND CHEMICAL PROPERTIES OF COS

Molecular weight:	60.07
Specific gravity, Gas:	2.1 (air = 1)
Density, liquid (-87 C):	1.24 g/ml
Vapor pressure (21 C):	9032 mm Hg
Melting point (1 atm):	-139 C
Boiling point (1 atm):	-50.2°C
1 mg/m^3 = 0.41 ppm (1 atm, 25 C)	
1 ppm = 2.5 mg/m^3 (1 atm, 25 C)	

COS is a linear molecule and has the structural representation

$$O = C = S \quad . \qquad (2)$$

Chemical Reactions

Carbon Disulfide

Synthesis--CS_2 is an industrially important organic chemical (Austin, 1974). Its production is limited to a vapor-phase reaction from methane and sulfur:

---

*Patty, F. A. (1963). Industrial Hygiene and Toxicology, 2nd ed., Vol. 2 (Wiley Interscience, New York, New York).

Fern, R. J. (1957), "The Chemistry of Carbonyl Sulfide, Chem. Rev., Vol. 57, p. 621.

$$CH_4 + 4S \xrightarrow[700^\circ C,\ 25\ psi]{\text{activated } Al_2O_3,\ Cr_2O_3} CS_2 + 2H_2S \quad . \qquad (3)$$

Hydrogen (H_2S) sulfide is reconverted to sulfur by the Claus process and recycled. An older process reacted surfur with wood charcoal in either a retort or an electric furnace.

In the reaction furnace of Claus plants for sulfur recovery systems, CS_2 is produced from COS and H_2S:

$$COS + H_2S \longrightarrow 2H_2S + CS_2 \qquad (4)$$

and from methane and sulfur:

$$CH_4 + 4S \longrightarrow 2H_2S + CS_2 \qquad (5)$$

Levels as high as 5000 ppm for both COS and CS_2 have been encountered in the tail gas of Claus plants; values ranging from 700-1500 ppm are more common.

An old process for the production of carbon tetrachloride used CS_2 and chlorine with an iron catalyst at ambient temperatures. Dithiocarbamates can result from reacting CS_2 with ammonia (Austin, 1974)*:

$$CS_2 + 2NH_3 \longrightarrow H_2NCSSNH_4 \quad . \qquad (6)$$

CS_2 has been detected in the magmatic gas over volcanoes (Nordlie, 1971),† during the aging of roasted coffee (Radtke et al., 1963),‡

---

*Austin, G. T. (1974), "The Industrially Significant Organic Chemicals--Part 2," Chem. Eng., p. 127 (February 18, 1974).

†Nordlie, B. E. (1971), "The Composition of the Magmatic Gas of Kilauea and Its Behavior in the Near Surface Environment," Am. J. Sci., Vol. 271, p. 417.

‡Radtke, R., et al., (1963) The Chemical Processes During the Aging of Roasted Coffee," Z. Lebensm. Untersuch. Forsch., Vol. 119, p. 293.

during the pressure cooking of grain-water mixtures (Ronkainen, 1973).* as a volatile constituent in the vapor of burning cigarettes (ORNL, 1975),* and in the vapor space above liquid sulfur (Pickren and Matson, 1964).‡

Decomposition--CS_2 is stable to hydrolysis in the pH region of environmental concern (pH = 4 to 10). Hydrolysis of carbon disulfide to carbon dioxide and hydrogen sulfide is a two-step process with carbonyl sulfide as an intermediate product:

$$CS_2 + H_2O \longrightarrow COS + H_2S \quad (7)$$

$$COS + H_2O \longrightarrow CO_2 + H_2S \quad (8)$$

$$CS_2 + H_2O \longrightarrow CO_2 + 2H_2S \quad (9)$$

At pH = 13 (0.1 N NaOH) CS_2 has a half-life of about 1 hour at 25 C. Extrapolation of this value to pH = 9 gives a half-life of 1.1 years. In basic solution, the carbon dioxide is converted to bicarbonate ($CO_2 + OH^- \longrightarrow HCO_3^-$), which precludes reversibility of the reaction. The electrophilic character of CS_2 does, however, provide for scrubbing and analytical techniques utilizing more nucleophilic reagents (amines and heterogeneous catalysts).

The flammability limits of CS_2 are 1 percent to 50 percent by volume in air, posing an acute fire and explosion hazard at high concentrations (flash point is -30 C). The oxidation has been studied

*Ronkainen, P. (1973), "Formation of Volatile Sulfur Compounds During Pressure Cooking of Grain-Water Mixtures," J. Inst. Brew., London, Vol. 79, No. 3, p. 200.

*ORNL (1975), "ORNL Tobacco Smoke Research Program Summary Report," Oak Ridge National Laboratory, March 1975.

‡Pickren, R. A., and R. F. Matson (1964), "Chromatograph Aboard a Liquid Sulfur Ship," Chem. Eng. Progr., Vol. 62, No. 2, p. 95.

for these as well as for theoretical purposes concerning the intermediate species in these reactions (Wood and Heicklen, 1971a).[6] Reports on the reaction with ozone and on photooxidation have also been made. The rate constant for the reaction of CS_2 with an oxygen atom is 5.6×10^9 $(M\text{-}sec)^{-1}$ at 25°C as calculated from the Arrhenius expression as obtained by Westenberg and DeHaas (1969).[*]

Olszyna and Heicklen (1970)[‡] have reported on the reaction of ozone with CS_2. The yields of products (normalized to initial ozone concentration) are 0.85 O_2, 0.36 SO_2, 0.16 OCS, 0.10 CO, and 0.03 CO_2.

Wood and Heicklen (1971b, 1973/74) have reported photooxidation studies of CS_2 at 2139 Å and 3130 Å. DeSorgo and coworkers (1965)[**] have also investigated this process. Photolysis at wavelengths less than 2300 Å proceeds in part by dissociation of the photoexcited species (CS_2^*) to CS and a sulfur atom:

$$CS_2 \longrightarrow CS_2^* \qquad (10)$$

$$CS_2^* \longrightarrow CS + S \qquad (11)$$

---

[6] Wood, W. P., and J. Heicklen (1971a), "Kinetics and Mechanism of the Carbon Disulfide Oxygen Explosion," J. Phys. Chem., Vol. 75, p. 861.

[*] Westenberg, A. A., and N. DeHaas (1969), "Atom-Molecule Kinetics Using ESR Detection, V Results for O + OCS, O + CS_2, O + NO_2 and H + C_2H_4," J. Chem. Phys., Vol 50, p. 707.

[‡] Olszyna, K. J., and J. Heicklen (1970), The Reaction of Ozone with Carbon Disulfide," J. Phys. Chem., Vol. 74, p. 4188.

[7] Wood, W. P., and J. Heicklen (1971b), "The Photooxidation of Carbon Disulfide," J. Phys. Chem., Vol. 75, p. 85.

[**] Wood, W. P., and J. Heicklen (1973/74), The Photooxidation of CS_2 at 2139 Å," J. Photochem., Vol. 2, p. 173.

[**] DeSorgo, M., et al., (1965), "The Photolysis of Carbon Disulfide and Carbon-Oxygen Mixtures," Can. J. Chem., Vol. 43, p. 1886.

In the presence of oxygen the products are CO, COS, SO_2, S_2O, and possibly SO_3. No carbon dioxide is found. At wavelengths greater than 2900 Å (lower energy) photodissociation does not occur. The mechanism is then the reaction of the photoexcited CS_2 with oxygen or itself:

$$CS_2^* + O_2 \longrightarrow CS + SOO \ (\rightarrow SO_2) \qquad (12)$$

$$CS_2^* + CS_2 \longrightarrow 2CS + S_2 \qquad (13)$$

An excited-state quenching process with O_2 was also in evidence:

$$CS_2^* + O_2 \longrightarrow CS_2 + O_2 \qquad (14)$$

The photooxidation study at 3130 Å is relevant to environmental conditions as this wavelength is within the solar spectrum. The products of the reaction were CO, COS, SO_2, and polymer (see Eqs. (15) and (16)) (Wood and Heicklen, 1971b). Carbon dioxide and SO_3 were not found as products. Quantum yields of products were small and ranged from 3×10^{-4} to 10^{-1}.

$$CS_2^* + O_2 \longrightarrow CS_2 + O_2$$

$$\longrightarrow CS + SOO \ (\rightarrow SO_2) \qquad (15)$$

$$CS + O_2 \longrightarrow COS + O$$

$$\longrightarrow CO + SO \ (\rightarrow SO_2) \qquad (16)$$

The product ratio COS/CO was found to be approximately 1:2 with a good carbon-sulfur mass balance for the gaseous products.

The information available indicates that CS_2 is relatively persistent in the atmosphere. Atmospheric oxidation of CS_2 will produce SO_2.

COS, and CO. In the absence of a direct measure of an environmental half-life for CS_2, we make the following estimates:

- Oxygen atom reaction. Modeling for atmospheric chemistry suggests that the oxygen atom is an important species which results from the photolysis of ozone and/or nitrogen dioxide among other sources (Demerjian et al., 1974).* If we assume an ambient steady-state concentration of oxygen atoms as 4×10^{-9} ppm (1.2×10^{-16} M), the half-life for CS_2 at 25°C is approximately 12 days.

- Ozone reaction. The data of Olszyna and Heicklen (1970) are not amenable to an environmental prediction. The unusual kinetic expression, as reported in the cited paper, has been explained as being due to aerosol formation in the experimental work (J. Heicklen, personal communication, 1975). Since the CS_2 concentrations in the experiment were in excess of 1300 ppm and the ozone concentration, the potential for aerosol formation under environmental conditions is not certain.

- Photooxidation of CS_2. To approximate the photooxidation of CS_2 some evaluation of the specific absorption rate constant at 3130 Å is needed (Leighton, 1961). Correcting the value for the SO_2 photooxidation study of Allen, McQuigg and Cadle (1972)† to that for CS_2 at this wavelength (extinction coefficient = 50 M^{-1} sec^{-1}) (Trieber et al., 1957),‡ a specific absorption rate constant of 0.93 day^{-1} is obtained. Taking the maximum quantum yield of 10^{-1} from the work of Wood and Heicklen (1971b), a mean lifetime of 130 hours is calculated, corresponding to 11 days when assuming 12 hours of sunlight per day.

---

*Demerjian, K. L., J. A. Kerr, and J. G. Calver (1974). "The Mechanism of Photochemical Smog Formation," Adv. Environ. Sci. Tech., Vol. 4, p. 1.

•Leighton, P. A. (1961). Photochemistry of Air Pollution (Academic Press, New York, New York).

†Allen, E. R., R. D. McQuigg and R. D. Cadle (1972). "The Photooxidation of Sulfur Dioxide in Air, Chemosphere, Vol. 1, p. 25.

‡Treiber, E. et al., (1957). "UV and IR-Absorption von Kohlenstoffdisselenid," Acta Chem. Scand. Vol. 11, p. 752.

Taking the minimum quantum yield value (3×10^{-3}), the mean lifetime is 10 years for 12 hours of sunlight per day.

Thus photooxidation may be a contributing or insignificant process in the degradation of CS_2 in the atmosphere. The uncertainty arises from both the limits of the experimental work reported (quantum yields, reactant concentrations, quenching effects, and the like) as well as the climatological conditions of any subject area.

Carbonyl Sulfide

Synthesis--COS is prepared by the action of oxidizing agents on CS_2 and as a by-product during the preparation of CS_2 from carbonaceous matter and SO_2. It may be formed by heating oxides of carbon with sulfur, or by the action of carbonyl chloride on sulfides. Fern (1957) reviews the various methods of synthesis. In the Claus reaction furnace, CO_2 reacts with H_2S:

$$CO_2 + H_2S \longrightarrow H_2O + COS \quad . \qquad (17)$$

Equations (7) and (16) indicate that COS is a natural decomposition product of CS_2 in the environment.

In a similar manner to CS_2, COS is produced in a variety of natural environs. It emanates from cattle manure at concentrations up to 3 ppm for several days (Elliot and Travis, 1973),* from volcanic fumaroles at temperatures exceeding 400°C (Momot, 1964),* during the cooking

---

*Elliot, L. F., and T. A. Travis (1973). "Detection of Carbonyl Sulfide and Other Gases Emanating from Beef Cattle Manure," Soil Sci. Soc. Am. Proc., Vol. 37, p. 700.

*Momot, J. (1964). "Carbonyl Sulfide, a Product of the Activity of Volcanic Fumaroles," Bull. Mens. Soc. Linnéenne Lyon, Vol. 33, No. 8, p. 326.

of grain-water mixtures (Ronkainen, 1973), and as a volatile component in tobacco combustion (ORSL, 1975). It is probable that most carbonaceous combustion processes involving sulfur compounds emit COS directly, as well as indirectly from biological production of H_2S, which further reacts with CO and CO_2 to produce COS.

Decomposition--COS is an intermediate in the hydrolysis of CS_2 as previously discussed. The half-life at pH = 12 (0.01 N KOH) is about three minutes at 22°C (Galivets et al., 1972).* Extrapolation to pH = 9 gives a half-life of about 2 days. At pH = 8 the half-life would be approximately 20 days. Its decomposition rate is more rapid than the hydrolysis of CS_2 under similar conditions. In 19 percent ethanol solvent, COS reacts some 1000 times faster than CS_2 in alkaline hydrolysis (Philipp and Dautzenberg, 1966).* A more detailed study on the alkaline hydrolysis of COS has also been reported by these authors (Philipp and Dautzenberg, 1965).

We found no photooxidation studies on COS or reports on reaction with ozone in the chemical literature. The rate of oxygen atom reaction with COS at 25°C as calculated from the work of Westenberg and DeHaas (1969) is 6.9×10^8 $(M \cdot sec)^{-1}$. Calculation at the same temperature based on the expression of Wood and Heicklen (1971b; 1973/1974) gives a rate constant of 3.6×10^8 $(M \cdot sec)^{-1}$:

$$COS + O \longrightarrow CO + SO \qquad (18)$$

---

*Galivets, L. S., Yu. I. Usatenko, and D. V. Galivets (1972), "Investigation of Kinetics of Alkaline Hydrolysis of Carbon Disulfide," Soviet Chem. Ind., Vol. 48, No. 12, p. 730.

*Philipp, B., and H. Dautzenberg (1965), "Untersuchungen zur Bildung und Zersetzung von Monothiocarbonat in wässeriger Lösung," Z. Physik. Chem. (Leipzig), Vol. 229, p. 210.

The volatility of COS and slow hydrolysis at relevant environmental pH values suggest that COS will be present and gradually degraded in the atmosphere. In the absence of other data, an environmental lifetime must be based on the oxygen atom reaction as previously discussed for CS_2. Again, if we assume a steady-state oxygen atom concentration of 1.2×10^{16} M and use the rate constant of Wood and Heicklen (1971b; 1973/1974), we calculate a half-life of 0.5 years. The value of Westenberg and deHaas (1969) would predict 0.3 years.

It has been suggested that COS elicits a toxic response due to partial decomposition in the lungs and blood stream to H_2S via hydrolysis (Patty, 1963). According to the above rate constants and chemical reviews by Fern (1957) this appears to be a relatively slow reaction at physiological pH. However, as indicated by Philipp and Dautzenberg (1966),* the hydrolysis of COS is 1000 times faster than CS_2 in an ethanol solvent. Thus, the production of H_2S in biochemical metabolism seems reasonable.

It is significant that in coke oven gas stored for five years a total disappearance of the O_2, COS, and CS_2 occurred. However, initial traces of iron and nickel carbonyl rose to 1000 mg/m^3 and 10 mg/m^3, respectively (Degent et al., 1962).

Environmental Exposure Factors

Sources and Emissions

Commercial Production and Emissions

Carbon Disulfide--In 1974 approximately 350 million kilograms of CS_2 were produced by five U.S. manufacturers. Over 80% of the production of CS_2 is used to make regenerated cellulose rayon and cellophane.

Degent, C., C. Rouse, and C. Lebras (1962), "Modification in Properties of Coke-Oven Gas During Underground Storage," Rev. Combust., Vol. 16, No. 1, p. 11.

* Philipp, B., and H. Dautzenberg (1966), "Zur Bildungsgeschwindigkeit von Na-Äthylmonothiocarbonat in Vergleich zu Na-Äthylxanthogenat," Z. Physik. Chem. (Leipzig), Vol. 231, p. 270.

In the rayon process CS_2 is employed as a solvent carrier to form xanthate crumb from alkali cellulose; H_2S and CS_2 are liberated upon immersion into acid spinning baths, where the viscose is coagulated and filaments extracted (Austin, 1974; Davidson and Feinleib, 1972[*]). The minor intermediate uses of CS_2 are numerous and include the manufacture of many industrial chemicals such as thiocarbamates, xanthates, mercaptans, thioureas, and carbon tetrachloride. Among the many dispersive uses, CS_2 is used as a solvent for oils, waxes, and the flushing of oil casings, and as a fumigant in pesticide applications (CEH, 1973).[*]

It is estimated that 100 million kilograms of industrially produced CS_2 were emitted in the U.S. to the atmosphere and approximately 35 million kilograms reached the water and land in 1973 (SRI, 1975).[‡] It is probable that the 35 million kilograms deposited to land and water found an eventual sink in the atmosphere due to the high volatility of the compound.

Carbonyl Sulfide--Less than one thousand pounds of COS were commercially produced in the United States in 1973 (Directory of Chemical Producers, 1975).[§] No dispersive uses are known, and the intermediate uses are in the synthesis of thioacids, 1-trisubstituted carbinols, and substituted thiazoles. The fraction of COS emitted to the environment by commercial sources is insignificant compared with that emitted by non-commercial sources (SRI, 1975); however, significant quantities are generated in the atmospheric decomposition of CS_2. COS was recently presented

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[*] Davidson, M., and M. Feinleib (1972), "Carbon Disulfide Poisoning: A Review," Am. Heart J., Vol. 83, No. 1, p. 100.

[*] CEH (1973), Chemical Economics Handbook (Stanford Research Institute, Menlo Park, California).

[‡] SRI (1975), "STAR Ranking Objective Subsystem," Draft Report, EPA Contract 68-01-2940, Task 023, Stanford Research Institute, Menlo Park, California.

[§] Directory of Chemical Producers (1975), Stanford Research Institute, Menlo Park, California.

as a chemical building block (Field and Sawhon, 1974)[6] and may find widespread use in the future.

Natural and Anthropogenic Emissions

The quantity of CS_2 and COS emitted from such natural sources as volcanic and geothermal activity is not known; however, previously cited reports indicate these natural sources may be significant contributors. As previously indicated, COS has been produced in large quantities (~) ppm air) from cattle feedlots. It also has been found in horseradish plant tissue up to 12 ppm (Rauch, 1962).[7] Combustion of fossil fuels and other carbonaceous material in the presence of sulfur compounds probably generates significant quantities and contributes to atmospheric emissions; however, the combustion contribution is probably disperse rather than concentrated. Various industrial gases have reported concentrations ranging from 30 ppm to 90 ppm COS and hydrogen produced from coal gas contains both COS and CS_2 (Ferm, 1957). Some NO_x reducing catalytic systems have been reported emitting COS from input SO_x (Koutsoukos et al., 1975).[8]

Of primary significance to the health and welfare of man are the sources where emissions of COS and CS_2 are most concentrated and controllable. Such emissions are found in sulfur recovery plants and potentially from mobile and stationary sources where reducing catalysts are used.

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[6] Field, E., and E. A. Sawhon (1974), "Carbonyl Sulfide as a Chemical Building Block," paper presented at the Symposium on New Sulfur Chemistry, 167th ACS National Meeting, Los Angeles, California, 1974.

[7] Rauch, G. (1962), "The Defensive Substances of Plants, III: Horse Radish Gas," Z. Naturforsch., Vol. 17, p. 800.

[8] Koutsoukos, E. P., et al. (1975), "Assessment of Catalysts for Control of NO_x from Stationary Power Plants," Report No. EPA-650/2-75-001-a, Environmental Protection Agency, Washington, D.C.

The process of removing sulfur-containing compounds (primarily H_2S) from gaseous fuels and recovering elemental sulfur as a by-product is a widespread activity in the United States. Sulfur recovery occurs mainly in conjunction with refinery operations and natural gas processing facilities and may also take place in certain types of chemical plants. Future expansion in all these areas may be expected to occur. In addition, the deployment during the next few decades of fossil fuel conversion facilities, such as coal liquefaction and gasification plants and oil shale processing plants, will greatly increase sulfur recovery activities.

The most common method of removing and recovering sulfur from hydrocarbon gas streams is to scrub the gas with amine compounds (e.g., monoethanolamine, di-isopropanolamine) to absorb the H_2S, after which the solution is stripped and the concentrated H_2S stream is directed to a Claus sulfur recovery unit where it is oxidized to elemental sulfur. The Claus process carries out catalytic oxidation of H_2S to sulfur in the presence of air at elevated temperatures. The important reactions in the Claus process are the direct oxidation reaction

$$H_2S + \frac{1}{2} O_2 \longrightarrow H_2O + S \qquad (19)$$

and the two-step process

$$H_2S + \frac{3}{2} O_2 \longrightarrow SO_2 + H_2O \qquad (20)$$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \qquad (21)$$

As many as three stages of Claus conversion may be used to remove up to 96 percent of the H_2S from the feed stream.

The formation of COS and CS_2 during the Claus process is due to the presence of carbon compounds. The amine scrubbing system removes

some CO_2 as well as hydrocarbons from the fuel gas and H_2S. The reactions which are thought to be important in the formation of CS_2 and COS during Claus conversion are:

$$CO_2 + H_2S \longrightarrow H_2O + COS \qquad (22)$$

$$COS + H_2S \longrightarrow H_2O + CS_2 \qquad (23)$$

$$CH_4 + 3S \longrightarrow 2H_2S + CS_2 \qquad (24)$$

The levels of COS and CS_2 present in the Claus tail gas stream thus depend on the quantities of CO_2 and hydrocarbons present in the feed stream. Typically, COS and CS_2 levels are on the order of 1000 ppm, although much higher levels may be attained (Beavon and Vaell, 1972).*

Typical practice in refineries and natural gas fields has been to incinerate the Claus tail gas, thus converting all reduced sulfur compounds to SO_2 and eliminating odor problems caused by H_2S and CS_2 emissions. However, the enactment of state and local laws regulating the emission of sulfur compounds (usually expressed as total sulfur) from sulfur recovery plants has brought about the increased use of tail gas cleanup procedures.

Tail gas treatment technologies generaly fall into two categories: those that oxidize the sulfur compounds in the tail gas to SO_2 and then apply SO_2 removal techniques, and those that reduce sulfur compounds to H_2S and then apply H_2S removal techniques. Examples of the former are the Wellman-Lord and IFP-2 processes. Examples of the latter

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* Beavon, D. K., and P. P. Vaell (1972), "The Beavon Sulfur Removal Process for Purifying Claus Plant Tail Gas," paper presented at the 37th Midyear Meeting, American Petroleum Institute Division of Refining, May 1972.

are the Cleanair, Beavon, and SCOT processes. Two other processes, IFP-1 and Sulfreen, are basically extensions of the Claus process and treat SO_2 and H_2S together.

Since incineration of the Claus tail gas leaves only trace amounts of COS and CS_2, the emission of these compounds becomes a problem only when tail gas treatment which deals with reduced sulfur compounds is applied. Only the Cleanair and Beavon processes emit any significant amounts of COS and CS_2 (tail gas of the SCOT process is incinerated). Both of these processes are effective in achieving greater than 99.9 percent sulfur removal in conjunction with an efficient Claus plant (Beavon and Vaell, 1972; Landrum et al., 1973).* However, emissions as high as 1000 ppm could occur with Beavon catalyst degradation.

As of January 1, 1974 there were 108 Claus sulfur recovery plants with an average capacity of 78.3 metric tons/day installed in the U.S. refineries (OGJ, 1974).† As of March 1, 1974, approximately 30 of these plants had installed or announced plans for tail gas treatment units.

Based on the total number (169) of Claus plants operating in the United States in early 1973 we estimate that approximately 60 Claus plants were associated with natural gas processing. The average capacity was approximately 127 metric tons/day (Beers, 1973).‡ There are also a few small sulfur recovery units operating in chemical plants.

The total level of sulfur recovery from all operations (refineries, natural gas processing, and chemical plants) was 16,053 metric tons/day in 1973 (Beers, 1973). Incinerations of tail gas resulting

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* Landrum, L. H., et al. (1973), "The Cleanair Sulfur Process," paper presented at the 74th AICLE Meeting, New Orleans, Louisiana, March 1973.

† OGJ (1974), Oil and Gas Journal, pp. 84-103 (April 1, 1974).

‡ Beers, W. D. (1973), "Characterization of Claus Plant Emissions," EPA Report No. EPA-72-73-188, Environmental Protection Agency, Washington, D.C. (April 1973).

from these operations would result in very small total emissions of COS and CS_2. Total emissions of SO_2 have been estimated at 135,000 metric tons per year, assuming no tail gas treatment (Beers, 1973).

Of the 30 Claus sulfur plants in refineries for which tail gas treatment units had been installed or planned in 1974, 16 were of the Cleanair or Beavon type (EPA, 1975),* both of which release CS_2 and COS. The total sulfur plant capacity for which these tail gas units were intended was approximately 1,828.8 metric tons/day, or 71 percent of the total sulfur recovery capacity for which tail gas cleanup units were installed.

As a basis for making a quantitative estimate of total emissions of CS_2 and COS we assumed first that emissions result only from Beavon or Cleanair units installed or planned for as of 1974 and that the proportion of these units installed in natural gas processing facilities is the same as the proportion installed in refineries. On this basis the total sulfur plant capacity of units having these tail gas treatment processes would be 3,487.4 metric tons/day. Assuming, on the average, that 2.0 kg/h CS_2 and 1.5 kg/h COS are emitted per 101.7 metric tons/day sulfur plant capacity with Cleanair or Beavon tail gas treatment (EPA, 1975), we calculate that 599.1 metric/tons CS_2 and 463.0 metric tons COS could have been emitted yearly from this source. Worst case conditions would assume Beavon catalyst degradation for all plants and would correspond to 20 kg/h CS_2 and 15.4 kg/h COS per 101.7 metric tons/day sulfur plant capacity.

If we assume that 71 percent of the entire 16,063.9 metric tons/day of U.S. sulfur plant capacity is equipped with Beavon or Cleanair units, then 1,997.2 metric tons CS_2 and 1,543.3 metric tons COS could be emitted yearly. Again, worst case conditions would correspond to 19,971.6 metric tons CS_2 and 15,432.6 metric tons COS emitted yearly.

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*EPA (1975), Environmental Protection Agency, unpublished data.

These figures do not take into account the anticipated expansion of sulfur plant capacity.

In coal conversion processes (gasification and liquefaction) the sulfur compounds in the coal are subjected to a reducing atmosphere so that H_2S, COS, and CS_2 are the primary sulfur compounds present in the product and by-product gas streams. In coal gasification processes, the first step is the reaction of coal with steam and oxygen at elevated temperatures and pressures. The resulting synthesis gas (mainly CO and H_2) is then quenched to remove particulates and oils subjected to the CO shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (25)$$

to achieve the appropriate H_2/CO molecular ratio, and finally reacted catalytically to form methane or substitute natural gas (SNG) as follows:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad (26)$$

The raw synthesis gas contains on the order of 3000-5000 ppm of H_2S, 100-1000 ppm of COS, and smaller amounts of CS_2 (<10 ppm) (EPA, 1974).* During the CO shift stage, much of the COS and CS_2 is hydrolyzed as follows:

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2 \qquad (27)$$

$$COS + H_2O \longrightarrow H_2S + CO_2 \qquad (28)$$

The remaining gas is then scrubbed to remove the acid gases CO_2 and H_2S as well as COS and CS_2. After stripping the scrubber solution, the resulting gas stream is dilute in H_2S compared with the concentrated streams

*EPA (1974), "Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology (May 1974, St. Louis, Missouri)," Report No. EPA-650/2-73-118, Environmental Protection Agency, Washington, D.C. (October 1974)

(90 percent H_2S) derived from refinery gases. If the stream is too dilute, the Claus process will have low efficiency in converting H_2S to sulfur. An alternative process which may be used is the Stretford process, where the H_2S is absorbed by a solution of sodium carbonate, sodium vanadate, and anthraquinone disulfonic acid. Through a series of steps, the overall oxidation reaction [Eq. (20)] is carried out. The Stretford process does not appreciably affect the COS and CS_2 present in the feed stream.

El Paso Natural Gas Company has proposed to build a coal gasification plant in northwestern New Mexico for the production of 76.2 million cubic meters (250 million cubic feet) per day of SNG. The Stretford process will be used to treat the H_2S resulting from scrubbing of the synthesis gas by the Rectisol (cold methanol) process. Both lean and rich H_2S streams will be generated and treated for sulfur recovery. The tail gas from the rich stream treatment will be incinerated, thus converting all sulfur compounds to SO_2. The tail gas from the lean stream treatment (containing mostly CO_2 and N_2) will be vented to the atmosphere. The concentrations of CS_2 and COS in this stream have been estimated at approximately 2 ppm and 65 ppm, respectively (El Paso, 1974).* The total level of emissions from the plant will be 2.7 kg/h CS_2 and 78 kg/h COS. These emission levels correspond to the release of 0.031 percent of the sulfur in the coal entering the plant as CS_2 and 0.57 percent of the sulfur as COS. The expected emission levels are based on thermodynamic calculations but are not well defined at this time, however.

In general, the release of COS and CS_2 from coal gasification plants will depend on the sulfur content of the coal being gasified, the methods chosen for gas purification and sulfur recovery, and the treatment (if any) applied to the sulfur recovery plant tail gas. The numbers presented above are based on the best current estimates according to El Paso's

*El Paso (1974), "Revised Report on Environmental Factors, Burnham Coal Gasification Project," El Paso Natural Gas Company, El Paso, Texas.

engineering design of a proposed commercial-size plant. Unfavorable reaction kinetics could result in emission several times the expected levels.

The generation of reduced sulfur compounds in coal liquefaction can occur in the following two processes: (1) the gasification of coal or by-product carbonaceous material to generate hydrogen for use in the hydrogenation step of coal liquefaction, and (2) the hydrogenation step itself, wherein finely divided coal, which has been slurried in a coal-derived solvent, is reacted with hydrogen to carry out dissolution of the organic matter in the coal.

The production of hydrogen from coal or other carbonaceous material proceeds much as in the production of SNG. The coal is gasified with steam and oxygen, the synthesis gas is quenched, and the CO shift reaction [Eq. (25)] is carried out. Of course, the extent of the CO shift reaction is much greater than it is when methane is the desired end product. Thus the degree of hydrolysis of CS_2 and COS may be expected to be greater. The subsequent purification of the H_2 stream to remove H_2S and CO_2, followed by sulfur recovery, will undoubtedly result in the release of lower quantities of CS_2 and COS per unit volume of gas produced, for the reasons cited above.

The hydrogenation of the coal slurry will generate primarily H_2S if pure hydrogen is employed. This H_2S will enter the by-product hydrocarbon gas stream, where purification and sulfur recovery will be carried out much as in refinery operations. CS_2 and COS will be formed primarily via reactions with hydrocarbons and CO_2 in the Claus plant.

An alternate route to coal hydrogenation has been considered in which synthesis gas would be used instead of hydrogen as the reducing medium (Exxon, 1975)*. In this case, the level of CS_2 and COS generated

*Exxon (1975), "Evaluation of Pollution Control in Fossil Fuel Conversion Processes--Liquefaction: Section 2, SRC Process," Report No. EPA-650/2-74-009-f, Exxon Research and Engineering Company (March 1975).

would be significantly higher, due to both the omission of the CO shift reaction (7), in which CS_2 and COS tend to be hydrolyzed, and the presence of CO and CO_2 in the hydrogenation medium, which leads to the formation of COS and CS_2.

The treatment of sulfur-containing by-product gases in oil shale retorting and upgrading plants will be similar to treatment carried out in refineries. A more dilute H_2S stream resulting from amine scrubbing of these gases will result, because of the high CO_2 content of the gases and the preferential absorption of CO_2 along with the H_2S. The dilute H_2S stream entering the Claus plant results in a lower overall sulfur recovery and possibly higher COS and CS_2 emissions in the tail gas after treatment. The Beavon or Cleanair processes are anticipated for the first commercial oil shale plants.

Colony Development Operation estimates that for a 50,000 bbl (5960 m^3) per day oil shale plant, 29 kg/h of sulfur compounds (such as SO_2) will be emitted in the 175 metric tons/day sulfur recovery plant tail gas (Colony, 1974).* This corresponds to a sulfur removal efficiency of 99.8 percent. Assuming that, on a volume basis, the tail gas sulfur is equally divided between COS and CS_2, we calculate that 11.8 kg/h CS_2 and 9.5 kg/h COS could be emitted as an upper limit from a 50,000 bbl per day oil shale plant.

Certain reducing catalysts for the control of NO_x also reduce SO_2 to S, H_2S, and COS. This is generally considered to be nonselective NO_x reduction and implies that sufficient reductant is present in the flue or exhaust gas streams to reduce all the oxidant constituents of the stream. An assessment of nonselective catalytic reduction as applied to stationary power plants is made by EPA (Koutsoukos et al., 1975). Some

*Colony (1974), "An Environmental Impact Analysis for a Shale Oil Complex at Parachute Creek, Colorado," Colony Development Operation, Atlantic Richfield Company.

reducing catalysts do not produce H_2S or COS while efficiently reducing NO_x and SO_2. No data were given for CS_2 production for any of the non-selective catalysts evaluated. It is probable that the residence times under the operating conditions in the catalytic processes reviewed were not sufficient for CS_2 generation. In some reported instances successful attempts were made to maximize simultaneous SO_2 reduction by increasing residence times; however, COS production dramatically increased together with noncollectable sulfur species other than elemental S or H_2S. A significant fraction was probably CS_2.

Of the nonselective reducing catalysts (that emit COS) reviewed in the EPA report, the most applicable to power plants appear to be TRW's NO_x - SO_x catalytic reduction process. In this process approximately six percent of input sulfur is reported emitted as COS. The remaining sulfur is emitted as elemental sulfur and H_2S.

An important reaction in Claus plant CS_2 production [Eq. (4)] combines COS and H_2S to form CS_2 and H_2O. Considering this reaction it is probable that some CS_2 is produced in nonselective reducing catalysts.

Estimates of Ambient Air Concentrations

Downwind ground-level concentrations can be estimated by a plume dispersion model (Perkins, 1974):*

$$X = \frac{Q}{\sigma_y \sigma_z U} e^{-\left[1/2\left(\frac{H}{\sigma_z}\right)^2\right]} \quad . \qquad (29)$$

where

X = μg COS and CS_2/m^3

Q = source strength in μg/sec

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*Perkins, H. C. (1974). Air Pollution. Chap. 8, "Plume Dispersion" (McGraw-Hill Book Company, New York, New York).

U = average wind speed in m/sec

σ_y, σ_z = vertical and horizontal diffusion coefficients in meters

H = effective height of source emission in meters.

Using a nomograph of Turner's (Perkins, 1974), the maximum ground-level concentration downwind from a 50-m stack under thinly overcast conditions and moderate windspeed (2-3 m/sec) would be approximately 2.5 km from the source. The value

$$\frac{e^{-\left[1/2\left(\frac{H}{\sigma_z}\right)^2\right]}}{\sigma_y \sigma_z}$$

reduces to $3.1 \cdot 10^{-5}$. Using U = 3 m/sec and Beavon catalyst degradation (20 kg/h CS_2 and 15.4 kg/h COS per 101.6 metric tons/day sulfur recovery plant: Q = $5.5 \cdot 10^6$ µg CS_2/sec and $4.3 \cdot 10^6$ µg COS/sec)

$$X = \frac{(3.1 \cdot 10^{-5})[(5.5 \cdot 10^6) \text{ or } (4.3 \cdot 10^6)]}{3}$$

$$= 57 \text{ µg } CS_2/m^3 \text{ and } 44 \text{ µg COS}/m^3$$

This would be the maximum ambient ground-level concentration occurring in any 1-h period. Average annual concentrations would be considerably lower.

It is of interest to consider what 1-h maximal ambient concentrations would be expected for an array of oil refinery sulfur recovery plants under inversion conditions. Perkins (1974) presents the following inversion model which can be adapted to summing refinery arrays:

$$X = \frac{Q}{(2\pi)^{1/2} U H_1 \sigma_y} \exp\left[\frac{1}{2}\left(\frac{Y}{\sigma_y}\right)^2\right] \quad (30)$$

where

H_i = upper level inversion layer

y = distance from horizontal plume axis.

Thus for a hypothetical array of nine sulfur recovery plants in rows of three at 3-km intervals, the sum of Eq. (31) for given values of y_i is performed to calculate X:

$$X = \frac{Q}{(2\pi)^{1/2} U H_i \sigma_{y_i}} \left[1 + 2e^{-1/2\left(\frac{y}{\sigma_{y_i}}\right)^2} \right] \qquad (31)$$

where

$\sigma_{y1} = f(d)$

$\sigma_{y2} = f(d + 3\ km)$

$\sigma_{y3} = f(d + 6\ km)$

$$X = \sum_{i=1}^{3} X_i$$

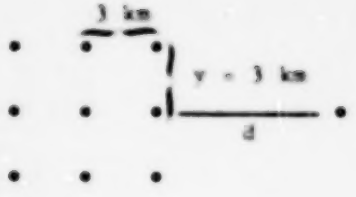

Table 3 presents the results for distances of 1, 5, 10, 20, and 100 km at an H_i of 400 meters, a U of 3 m/sec, and a Q of 20 kg/h CS_2 ($5.6 \cdot 10^6$ μg/sec) and 15.4 kg/h COS ($4.3 \cdot 10^6$ μg/sec), corresponding to emissions from a 101.7 metric tons/day sulfur recovery plant with Beavon catalyst degradation.

The predicted ambient values are directly related to emission rates with this model.

Table 3

ESTIMATED ONE-HOUR AMBIENT INVERSION CONCENTRATIONS OF CS_2 AND COS AT VARIOUS DISTANCES FROM A HYPOTHETICAL ARRAY OF SULFUR RECOVERY PLANTS

	1 km	5 km	10 km	20 km	100 km
$\mu g/m^3$ CS_2	22	12	7	4	2
$\mu g/m^3$ COS	24	9	5	3	1

It is also of interest to compute what ambient levels of CS_2 or COS could exist within a defined basin during a period of stagnation. The following simple model can be used to calculate the potential ambient levels from sulfur recovery plants:

$$X = \frac{TPFQ'(1 - L)}{AH_i} \tag{32}$$

where

X = $\mu g/m^3$

T = hours of stagnation

P = total sulfur recovery capacity (metric tons/day)

F = fraction emitting CS_2 and COS

Q' = emission rate ($\mu g/h$ 102 metric tons/day)

L = fraction lost from basin

A = area of basin (m^2)

H_i = height of inversion (m).

Substituting the following values, we can approximate for the Los Angeles Basin the input from sulfur recovery plants under worst operating conditions (Beavon catalyst degradation):

$T = 120$ hours

$P = 2033.4$ metric tons/day

$F = 0.7$

$Q' = 2.0 \cdot 10^{10}$ μg CS_2/h (20 kg/h) or $1.5 \cdot 10^{10}$ μg COS/h (34 μg/h)

$L = 0.1$

$A = 1.55 \cdot 10^9$ m^2 (15 miles by 40 miles)

$H_i = 300$ m

$$X = \frac{(120)(2033.4)(0.7)\left(\frac{2 \cdot 10^{10}}{100}\right)(0.9)}{(1.55 \cdot 10^9)(3 \cdot 10^2)}$$

$$= 65 \text{ μg } CS_2/m^3 \quad \text{or} \quad 48 \text{ μg COS}/m^3$$

From 1973 data, we estimate 136 million kg ($1.4 \cdot 10^5$ metric tons) of CS_2 are emitted to the atmosphere annually from industrial production for intermediate and dispersive commercial use. Assuming that this commercial emission is evenly distributed with respect to the population, the stagnation level for the Los Angeles Basin can be calculated in a manner as for sulfur recovery plant emissions:

$$X = \frac{ED\,F_p\,(1 - L)}{AH_i} \tag{33}$$

where

$X = \mu g/m^3$

E = daily national emission rate (μg/day)

D = days of stagnation

F_p = fraction of population

L = loss during inversion

A = area of basin

H_i = height of inversion

Substituting the following values:

$$E = 3.73 \cdot 10^{14} \text{ } \mu g/day \quad (1.4 \cdot 10^{5} \text{ metric tons}/365 \text{ days} \cdot 9.08 \cdot 10^{11} \mu g/\text{ton})$$

$$D = 5 \text{ days}$$

$$F_p = 0.036 \quad (7.5 \text{ million})$$

$$L = 0.1$$

$$AH_1 = 4.65 \cdot 10^{11} \text{ } m^3$$

$$X = \frac{(3.73 \cdot 10^{14})(5)(0.036)(0.9)}{4.65 \cdot 10^{11}}$$

$$= \frac{6.04 \cdot 10^{3}}{4.65 \cdot 10^{11}}$$

$$= 129 \text{ } \mu g/m^3 \text{ } CS_2$$

Emissions of COS and CS_2 to the Los Angeles Basin from other sources are difficult to estimate; a preliminary appraisal of the quantity of sulfur flowing through the different fuel processes is required before such emissions can be estimated. Table 4 presents the sources of California's primary energy supply.

We do not consider gas, wood, hydroelectric, and nuclear primary energy supplies because they are not a source of sulfur emissions. Nor do we consider coal, because it is not a significant part of California's (and Los Angeles') energy supply or sulfur emissions.

Table 5 presents data concerning the sales of heating oils and sulfur content in California.

Table 4

CALIFORNIA TOTAL PRIMARY ENERGY SUPPLY: 1971

	10^{15} Joules (Trillion BTU)		Percentage of Total
Petroleum	3120.0	(2971.4)	50.92%
Coal	50.7	(48.3)	0.83
Gas	2480.0	(2361.9)	40.48
Wood	15.6	(14.9)	0.26
Hydroelectric	422.3	(402.2)	6.89
Nuclear	38.0	(36.2)	0.62
	6126.6	(5834.9)	100.00%

Source: SRI (1973)*

Table 5

CALIFORNIA SALES OF HEATING OILS

Type	10^3 Barrels	Product kg/ Barrel	Wt Percent S	Metric Tons of Sulfur
#1 Distillate	497	129.7	0.088	5.7
#2 Distillate	3059	135.2	0.230	951.6
#4 Distillate	730	149.7	1.090	1,191.8
#5 Distillate	296	153.8	1.330	605.8
#6 Distillate	2873	156.5	1.640	7,378.3
	7455			10,133.2

Sources: NPN (1975)*; Bureau of Mines (1974)† for average sulfur content

*SRI (1973), "Meeting California's Energy Requirements, 1975-2000," SRI Project ECC-2355, Stanford Research Institute, Menlo Park, California.

*NPN (1975), National Petroleum News Factbook (May 1975).

†Bureau of Mines (1974), Burner Fuel Oils, 1974," Mineral Industrial Surveys, Bureau of Mines, Petroleum Products Survey, Nos. 82, 86, and 88.

These petroleum products are consumed in residential and commercial space heating. The most recent census data assign 33 percent of California's total population to the Los Angeles-Long Beach metropolitan area.* Southern California has only half the degree-day heating requirement of northern California (SRI, 1973). It is reasonable, then, to estimate the sulfur burden in the Los Angeles SMSA from heating oils at

$$10{,}133.2 \times 0.33 \times 0.5 = \frac{1672.0 \text{ metric tons of sulfur}}{\text{year}}$$

The sales of distillate and residual fuel oils in all applications other than space heating in California are summarized in Tables 6 and 7, along with their sulfur burden. We assigned the grades of product used by each listed user, since the Bureau of Mines data do not so differentiate.

Some users in California do not burden the Los Angeles area atmosphere with all of their sulfur (e.g., vessel bunkering). Other users have integrated capability to some degree to remove the sulfur from the combustion products (e.g., oil company uses). Selection of users was not in the scope of work for this study, so the aggregate sulfur burden is not estimated. The applicable fractions for the Los Angeles SMSA for any of the user categories that might be selected are the population fraction (Los Angeles' population in relation to southern California's population) and the activity fraction (southern California's fraction of California's industrial activity as measured by value added in manufacture)(SRI, 1973). Thus, 0.55 (population fraction) × 0.64 (activity fraction) = 0.35. 0.35 × sulfur content for selected user = sulfur burden.

Table 8 presents the Los Angeles SMSA sales and average sulfur content of gasoline.

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*12/27 data from Sales Management, July 27, 1973.

Table 6

CALIFORNIA SALES OF DISTILLATE-TYPE FUEL OILS AND AVERAGE SULFUR CONTENT: 1973

Use	10^3 Barrels	Product kg/Barrel	Wt. Percent S	Metric Tons of Sulfur
Industrial	5,570	133	0.32	2370.4
Oil company	903	133	0.32	384.3
Railroads	8,530	134	0.315	3597.9
Vessel bunkering	2,210	133	0.32	940.4
Military	5,605	133	0.32	2385.3
Electric utilities	888	133	0.32	377.9
On highway	18,415	133	0.265	6490.0
Off highway	4,278	133	0.32	1820.6
Other	480	133	0.32	204.3

Sources: Bureau of Mines (1973,* 1974)

Table 7

CALIFORNIA SALES OF RESIDUAL-TYPE FUEL OILS AND AVERAGE SULFUR CONTENT: 1974

Use	10^3 Barrels	Product kg/Barrel	Wt. Percent S	Metric Tons of Sulfur
Industrial	6,466	154	1.33	13,232.6
Oil company use	5,495	156	1.64	14,112.0
Railroads	54	154	1.33	110.5
Vessel bunkering	19,356	156	1.64	49,709.4
Military	1,134	154	1.33	2,318.0
Electric utilities	84,183	156	1.64	216,195.9
Other	202	154	1.33	413.4

Sources: Bureau of Mines (1973, 1974)

*Bureau of Mines (1973), "Fuel Oil Sales, Annual, 1973."

Table 8

LOS ANGELES SMSA SALES OF GASOLINE AND
AVERAGE SULFUR CONTENT: 1974

Grade	10^3 Barrels	Product kg/Barrel	Wt. Percent S	Metric Tons of Sulfur
Premium price	44,310	117.9	0.033	1725.6
Regular price	39,770	118.3	0.057	2685.5
				4411.1

Source: NPN (1975); Bureau of Mines (1974)

The sulfur burden for Los Angeles from motor gasoline is therefore 4411.1 metric tons of sulfur.

Table 9 summarizes the estimated daily emissions of sulfur and potential COS and CS_2 emissions if mobile and stationary nonselective reducing catalysts are used in the Los Angeles area. Using the sum of the estimated emission rates for COS and CS_2, we can calculate the stagnation level in a similar manner as in Eqs. (32) and (33):

$$X = \frac{ED\ (1 - L)}{AH_1} \quad . \tag{34}$$

Substituting the following values for electric utilies and automobile sources:

$E = 1.4 \cdot 10^{13}$ g COS/day, and $6.7 \cdot 10^{11}$ g CS_2/day

$D = 5$ days

$L = 0.1$

$AH_1 = 4.65 \cdot 10^{11}\ m^3$

Table 9

TOTAL SULFUR CONSUMPTION AND EMISSION AND ESTIMATED CONVERSION TO COS AND CS_2

Use	Sulfur Consumption Emission (g/day)	Conversion Factor*		Estimated Emission Rate (g/day)	
		COS	CO_2	COS	CO_2
Heating oils	4.6×10^{12}	--	--	--	--
Electric utilities	2.1×10^{14}	0.06	0.003	1.3×10^{13}	6.3×10^{11}
Automotive gasoline	1.2×10^{13}	0.06	0.003	0.7×10^{12}	3.6×10^{10}
Others†	4.6×10^{13}	--	--	--	--

*Assuming stationary/mobile nonselective reducing catalysts installed
CS_2 emission estimated as 0.1 of COS as sulfur

†Industrial, oil companies, railroads, military, highway.

$$X = \frac{(1.4 \cdot 10^{13}\ \mu g\ COS/day\ and/or\ 6.7 \cdot 10^{11}\ \mu g\ CS/day)(5)(0.9)}{4.65 \cdot 10^{11}\ m^3}$$

$$= 135\ \mu g\ COS/m^3 \text{ and } 6.5\ \mu g\ CS_2/m^3$$

Table 10 summarizes all the contributing sources to the Los Angeles stagnation levels of COS and CS_2 under the assumptions previously given.

It should be noted that the values used in the above cases approximate near worst case conditions. Actual averages over longer time periods (e.g., one year) would be considerably lower.

Table 10

SUMMARY OF SOURCE CONTRIBUTION TO ESTIMATED AMBIENT STAGNATION LEVELS

Source	Estimated Ambient Stagnation Levels ($\mu g/m^3$)	
	CS_2	COS
Refinery sulfur recovery plants	65	48
Electric utilities*	6	128
Automotive gasoline*	0.3	7
Commercial applications	129	--
Total	200	183

*Nonselective reducing catalyst.

Health and Welfare Effects

As previously noted, CS_2 is used as an industrial chemical primarily in the cold vulcanization of rubber and the manufacture of viscose rayon. Acute and chronic human exposures have occurred in the industrial workplace, providing a broad range of health effect documentations and encouraging continuing research programs to establish threshold limits. Conversely, COS has received little application as an industrial chemical; thus records of human exposures are few, and health effects studies are all but absent from the literature. However, because of the similarity in chemical and physical properties, as well as some reports that COS is a potentially toxic biological metabolite of CS_2, some analogies may be inferred between the two substances.

As mentioned above, extensive documentation on the health and welfare effects of CS_2 are present in the literature. These include a number of review articles and three international symposia. The World Health Organization (WHO) will soon be issuing a final report on CS_2 following review by appropriate government and industrial health organizations. Aside from the WHO document, reviews to note are those by Brieger and Teisinger (1967)* on the First International Symposium; a review of the Third International Symposium (Lieben, 1974);* a Yant Memorial Lecture (Teisinger, 1974);§ and general literature reviews by Patty (1963).

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* Brieger, H., and J. Teisinger (1967). Toxicology of Carbon Disulfide (Excerpta Medica Foundation, New York, New York).

* Lieben, J. (1974). "Third International Symposium on Toxicology of Carbon Disulphide." Arch. Environ. Health, Vol 29, p. 173.

§ Teisinger, J. (1974). "1972 Yant Memorial Lecture--New Advances in Toxicology of Carbon Disulfide." Am. Ind. Hyg. Assoc. J., Vol. 35, No. 2, p. 55.

Browning (1965),[°] Hamilton and Hardy (1974),[•] and Davidson and Feinleib (1972). The following paragraphs are syntheses of the above reviews with current research findings.

Absorption, Excretion, Metabolism

CS_2 in inspired air enters the blood by way of the alveoli. It is quite soluble in fat, miscible with alcohol, ether, and benzene, and relatively insoluble in water. An equilibrium (total body saturation) can be achieved within two hours upon inhalation of levels from 17 to 30 ppm. Eighty percent of inhaled CS_2 is sorbed within the first 15 minutes and 95 percent in two hours (Teisinger and Soucek, 1949).[§] Red blood cells take up twice as much CS_2 as the plasma (McKee, et al. 1943),[‡] and the fat-soluble property allows distribution to all tissues (Brieger, 1961).[••]

Blood levels of CS_2, following exposure, fall 75 percent in one hour and almost to zero in two (Teisinger and Soucek, 1949). McKee (1941)[••] found that complete desaturation requires about three to eight hours and is directly related to the level of exposure. Metabolic degradation accounts for approximately 95 percent of the loss of free CS_2, while

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[°] Browning, E. (1965). Toxicity and Metabolism of Industrial Solvents (Elsevier Publishing Company, New York, New York).

[•] Hamilton, A., and H. L. Hardy (1974). Industrial Toxicology, 3rd ed. (Publishing Sciences Group Inc., Acton, Massachusetts).

[§] Teisinger, J., and B. Soucek (1949). "Absorption and Elimination of Carbon Disulfide in Man," J. Ind. Hyg., Vol. 31, p. 67.

[‡] McKee, R., et al.(1943). "A Solvent Vapor: Carbon Disulfide--Absorption, Elimination, Metabolism and Mode of Action," J. Am. Med. Assoc., Vol. 122, p. 217.

[••] Brieger, H. (1961). "Chronic Carbon Disulfide Poisoning," J. Occup. Med., Vol. 3, p. 302.

[••] McKee, R. (1941). "Solubility of Carbon Disulfide Vapor in Body Fluids and Tissues," J. Ind. Hyg., Vol. 23, p. 151.

excretion via the lungs and kidney account for 5 and 0.05 percent, respectively (Teisinger and Soucek, 1949). Other research indicates that from 10 percent to 30 percent is exhaled, and 1 percent is excreted in urine (Brieger, 1961).

The metabolic products of CS_2 in human metabolism are not thoroughly known. Dithiocarbamates are the products of the reaction of CS_2 with amino acids (Brieger, 1961) and have been found in the blood (Scheel, 1967);[c] thiocarbamide has been found in the urine of exposed workers. Thiourea and 2-mercapto-2-thiazolinone-5 have also been identified in the urine (Pergal et al., 1972).[d]

From comprehensive studies on the metabolism of CS_2 by Soucek and Zahradnik, Davidson and Feinleib (1972) proposed that sorbed CS_2 combines with materials containing a free amine group or basic nitrogen atom. Thus products of the reaction of CS_2 with proteins contain an increased number of sulfhydryl groups.

There are several mechanisms regarding the toxic action of CS_2. These involve the interaction of CS_2 or its metabolites with proteins, fats, and coenzymes. Simon (1961)[e] has suggested that CS_2 is a universal enzyme inhibitor that disturbs oxidative phosphorylation and fat metabolism.

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[c] Scheel, L. (1967). "Experimental CS_2 Poisoning in Rabbits, Its Mechanism and Similarities with Human Case Reports," in Toxicology of Carbon Disulfide, H. Brieger and J. Teisinger, eds., pp. 107-114 (Excerpta Medica Foundation, New York, New York).

[d] Pergal, M., et al. (1972). "Carbon Disulfide Metabolites Excreted in the Urine of Exposed Workers," Arch. Environ. Health, Vol. 25, p. 38.

[e] Simon, K. (1961). "Chronische Vergiftung durch Schwefelkohlenstoff," Med. Monatschr., Vol. 16, p. 810, cited in Toxicity and Metabolism of Industrial Solvents, E. Browning, ed., p. 704 (Elsevier Publishing Company, New York, New York).

Cohen et al. (1959)* propose that the thiocarbamates and other metabolites with sulfhydryl groups chelate metal ions and interfere with the energy metabolism of cells. The stress incurred promotes a mobilization of fat stores and leads to a disturbance of cellular metabolism and cell injury or death. Disturbances in zinc metabolism following CS_2 exposure have been observed by Scheel (1967), and decreases in serum zinc and increases in urinary zinc in exposed workers have been observed by El Gazzar and associates (1973).† Many enzymes require metal ions as activators (e.g., Zn and Mg for alkaline phosphatase); thus the chelating effect of sulfhydryl-bearing metabolites of CS_2 to metal ions would inhibit the enzymes from performing their normal function. Scheel (1967) has noted decreased toxic effects of CS_2 in animals fed highly mineralized diets.

Mack et al. (1974)‡ found inhibition of oxidative N-demethylation in man at doses as low as 10 ppm CS_2 for six hours. The inhibition was reversible and the deficit in metabolism was gradually compensated after exposure ceased. The inhibitory mechanism is not known. However, as in the above studies, the CS_2 metabolites, which are proposed to have similar structures as dithiocarbamates, become active in enzymes due to chelation of catalytically active metals. Mack et al. state, however, that a reverse route is conceivable, in which the metabolites (e.g., dithiocarbamates) release CS_2, providing an indirect reaction with mixed-function oxidases and other enzymes.

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* Cohen, et al. (1959), "Biochemical Mechanisms in Chronic Carbon Disulfide Poisoning," Am. Ind. Hyg. Assoc. J., Vol. 20, p. 303.

† El Gazzar, et al. (1973), "Changes in Zinc and Serum Proteins Due to Carbon Disulfide Poisoning," Brit. J. Ind. Med., Vol. 30, p. 284.

‡ Mack, T., K. Freundt, and D. Henschler (1974), "Inhibition of Oxidative N-Demethylation in Man by Low Doses of Inhaled Carbon Disulfide," Biochem. Pharmac., Vol. 23, p. 607.

Vigliani (1954)° reports that under chronic exposures to CS_2, a persistent presence of lipoproteinic macromolecules leads to hyalinization and carbon disulfide arteriosclerosis. Vigliani implicated a disturbance of the lipaemia clearing factor. In his exposed subjects, he noted greater incidences of hypertension and vascular spasms, which were correlated with an increase in the ratio of beta to alpha lipoproteins. Cohen et al. (1959) also noted the same increases in beta to alpha lipoproteins but attributed the results to stress rather than to an inhibition of the lipaemia clearing factor.

A study of 120 viscose rayon workers cited a 34 percent increase over normal of serum cholesterol, and the results were confirmed using dogs as experimental animals (Davidson and Feinleib, 1972).

The effects of CS_2 on Vitamin B6 metabolism have been studied extensively and there is a significant similarity in the neurological symptoms of B6 deficiency and CS_2 poisoning (Davidson and Feinleib, 1972). Increased diets of Vitamin B6 have been shown to inhibit toxic effects of CS_2 in animals (Teisinger, 1974). Teisinger feels that nervous system lesions due to CS_2 poisoning are associated with the inhibition of monoamine oxidase activity and the accumulation of serotonin in the brain. This mechanism is not widely supported, however, because there is contradictory evidence in the literature. Browning (1965) suggests another mechanism involving chelation of copper by thiocarbamates in nerve cells, resulting in inhibition of the functions of cytochrome oxidases and coenzyme-A dehydrogenase.

°Vigliani, E. C. (1954). "Carbon Disulfide Poisoning in Viscose Rayon Factories." Brit. J. Ind. Med., Vol. 11, p. 235.

The liver is an important organ in the metabolism of CS_2. Dalvi et al. (1974,* 1975*), using radio labeled CS_2, have revealed that COS is formed from CS_2 when incubated with rat liver microsomes in the presence of NADPH. Furthermore, the COS is metabolized to yield sulfur radicals and CO_2. Each step appears analogous to a mixed-function oxidase catalysis and leads to formations of highly reactive sulfur radicals that covalently bind to microsomal membranes and decrease the concentration of cytochrome P-450. This highly reactive sulfur leads to a decrease in the concentration of cytochrome P-450 and hepatic damage seen on liver examinations following CS_2 administration to rats. Thus, if oxidative metabolism plays a significant role in the toxicity of CS_2 (forming reactive sulfur atoms), COS would likewise be expected to be toxic.

Unfortunately, we have not uncovered in the literature any research describing the mechanism of toxicity of COS, other than the formation of a reactive sulfur species in liver microsomes. However, assuming oxidative metabolism is the eventual cause of toxicity for CS_2 and COS (due to the formation of highly reactive sulfur atoms), then on a molecular level one molecule of CS_2 would be twice as toxic as one molecule of COS. This is an oversimplification of the toxicity problem for the whole organism, due to the confounding of probable differences in tissue distribution, metabolism, and the formation of toxic metabolites. However, because of the lack of data concerning chronic COS toxicity, we hypothesize the 2:1 (CS_2:COS) toxicity ratio.

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*Dalvi, R. R., et al. (1974). "Studies of the Metabolism of Carbon Disulfide by Rat Liver Microsomes." Life Sci., Vol. 14, p. 1785.

*Dalvi, R. R., et al. (1975). "Toxicological Implications of the Mixed-Function Oxidase Catalyzed Metabolism of Carbon Disulfide." Chem. Biol. Int., Vol. 10, p. 347.

Toxic Effects

Although CS_2 is highly volatile, a case of acute poisoning by ingestion, followed by death within four hours, occurred in a victim who swallowed a glass of CS_2 (Foreman, 1886).* Physical examination prior to death showed normal pupils, abnormal respiration, and a rapid pulse (150-160/minute). Some studies on the acute toxicity of COS in animals have been reported and are presented in Table 11 along with CS_2 data.

Table 11

LETHAL DOSES OF CS_2 AND COS (INHALATION)

Species	CS_2 (ppm)	Death (Time)	COS (ppm)	Death (Time)
Man (Patty, 1963)	4,815	30 min		
Cats (Browning, 1965)	1,260	180 min		
Rabbits (Patty, 1963)			3,200	60 min
Mice (Patty, 1963)			8,900	0.75 min
Mice (Patty, 1963)			2,900	1.5 min
Mice (Patty, 1963)			1,200	35 min
Rats (Hayashi et al., 1971)*			5,000	10 h
Rats (Hayashi et al., 1971)			20,000	45 min

*Hayashi, E., et al. (1971). "Acute Toxicity of Carbonyl Sulfide Towards Animals." Oyo Yakuri, Vol. 5, No. 3, p. 435.

In acute exposures, COS and CS_2 act upon the central nervous system and result in death by respiratory paralysis. Chronic toxicity studies with animals for COS have not been found in the literature and exposure of humans has not been recorded.

*Foreman, W. (1886). "Notes of a Fatal Case of Poisoning by Bisulphide of Carbon," Lancet, Vol. 2, p. 118.

Experimental studies of CS_2 on animals reveal a wide variety of changes involving the nervous, reproductive, and cardiovascular systems, and the liver, kidney, and blood.

Chronic exposure in man, likewise, has caused a variety of effects. Most noticeable are those on the nervous system; potentially the most dangerous effects are those on the heart, which have led to an increased incidence of coronary heart disease.

In the 1850s the French were aware of the public health aspects of respired CS_2 and diagnosed over 80 cases of "carbon disulfide neurosis" (a wide variety of nervous and mental disorders with an early stage of excitation followed by a second stage of depression) in the rubber industry, where CS_2 was used. These findings were confirmed with animal studies. Other symptoms of CS_2 intoxication reported in the early literature were classified as "CS_2 insanity," "mental morbidity," "chronic neuritis," and "acute mania." Among rubber workers in 1898, "mental morbidity" was reported to have decreased by 86 percent ten years after improvements in ventilation that decreased CS_2 concentrations from several hundred to less than 30 ppm (Davidson and Feinleib, 1972).

The effect of CS_2 on the central nervous system is now generally considered as polyneuritic (affecting a large number of spinal nerves). Recent neurophysiological studies of chronically poisoned workers (exposed to 20-40 ppm in the 1950s and 10-30 ppm in the 1960s) indicate impairments at several levels of the central and peripheral nervous system (Seppäläinen et al., 1972).* The exact locus of the polyneuropathic type of lesion varies. Of 9, 17, and 10 subjects exposed (from 0.5 to 2 years,

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*Seppäläinen, A. M., et al. (1972). "Neurophysiological Findings in Chronic Carbon Disulfide Poisoning, A Descriptive Study." Work-Environm. Health, Vol. 9, p. 71.

3 to 10 years, and greater than 10 years, respectively); 0, 3, and 1 subjects were neurophysiologically normal, compared with a control group of 120 normal adults. The reported observations show that the effect of CS_2 on the nervous system cannot be considered specific.

Tiller and coworkers (1968)* found that in men with more than 10 years employ in the viscose rayon industry, the death rate from coronary heart disease (CHD) was 2.5 times greater in exposed workers than in nonexposed workers. Nearly half of the air-monitoring samples over a period of 16 years reported levels greater than 20 ppm. It is interesting to note that the nonexposed rayon workers had a significantly higher observed death rate than expected for CHD, as had other local men who were not employed in the viscose rayon industry. The male death rate from cardiovascular diseases in those areas of England and Wales where viscose rayon factories are situated is somewhat higher than the national rates but is thought to be due to soft drinking water. (Soft drinking water frequently acquires high concentrations of heavy metals, which have been cited as contributors to CHD.)

Hernberg and coworkers (1970)† reported an excess of coronary deaths among 48 men who had been exposed to CS_2 for at least five years and had died under the age of 65. The expected number of deaths from CHD was 15; however, 25 were observed. Examination of 343 viscose rayon workers, who were matched with 343 control subjects from a paper mill revealed that the subjects exposed to CS_2 had higher blood pressure and a slightly

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*Tiller, J. R., R. Schilling, and J. Morris (1968), "Occupational Toxic Factor in Mortality from Coronary Heart Disease," Brit. Med. J., Vol. 4, p. 407.

†Hernberg, S., et al. (1970), "Coronary Heart Disease Among Workers Exposed to Carbon Disulphide," Brit. J. Ind. Med., Vol. 27, p. 313.

higher prevalence of electrocardiogram abnormalities. Exposures to CS_2 were from 20 ppm to 40 ppm in the 1950s and about 10 ppm to 30 ppm in the 1960s.

A follow-up study by Hernberg and coworkers (1973)[a] on the 343 exposed workers showed that 16 men had died from CHD compared with 3 in the control cohort over a five-and-one-half year period. Other causes of death were evenly distributed (7 and 6) among both groups. The control cohort had an incidence of CHD that was less than the national death statistics (Finland), and this was attributed to the occupational status. The incidence of CHD mortality was 6.7 percent and 2.6 percent for the two groups. A further analysis of the data of Hernberg and coworkers indicated that 11 nonfatal first cardiac infarctions had occurred in the exposed group as compared with 4 in the control (Tolonen et al., 1975).[b] The exposed group also had a greater prevalence of angina (chest pains).

Lieben and coworkers (1974)[c] evaluated the effects of the CS_2 on the cardiovascular system of 1498 presently employed U.S. rayon workers compared with 481 acetate workers. An electrocardiogram, blood pressure, total cholesterol, and occupational exposure history were obtained for each worker. The only statistically significant finding was a higher blood pressure (140/87) in workers in the rayon plants than in workers in the acetate plant (135/83).

The question of whether the association between CHD and CS_2 is causal is still addressed, although the circumstances favor such an association. Some biochemical mechanisms that add credence to the causality are decreases in fibrinolytic activity (Brieger and Teisinger, 1967),

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[a] Hernberg, S., et al. (1973), "Excess Mortality from Coronary Heart Disease in Viscose Rayon Workers Exposed to Carbon Disulfide," Work-Environ.-Health, Vol. 10, p. 93.

[b] Tolonen, M., et al. (1975), "A Follow-up Study of Coronary Heart Disease in Viscose Rayon Workers Exposed to Carbon Disulfide," Brit. J. Ind. Med., Vol. 32, p. 1.

[c] Lieben, J., et al. (1974), "Cardiovascular Effects of CS_2 Exposure," J. Occ. Med., Vol. 16, No. 7, p. 449.

changes in lipid metabolism, elevation of blood pressure, and myocardial effects through interference with catecholamine metabolism (Magos, 1974).*

Another notable toxic effect of CS_2 is on the reproductive system. The estrous cycle of rats was found distorted (Vasileva, 1973).† Follow-up studies on women workers exposed to greater than 10 ppm and 5 ppm CS_2 indicated greater disruption of the menstrual cycle and more pathological changes in the cellular composition of vaginal smears than in the control groups. Humans (Lancranjan, 1972)‡ and rats have been shown to have changes in spermatogenesis (Rozewichi et al, 1973).§

A synergism between CS_2 (20-25 ppm) and H_2S (20-25 ppm) has been noted in rabbits exposed for four hours per day for 150 consecutive days (Kuwai, 1960).** In the mixed gases group, reticulocyte count and globulin increased, and total cholesterol rose on the 110th day and continued to rise for the remainder of the experiment. No abnormality was detected in the separate groups except for a slight elevation of total cholesterol in the H_2S group, which eventually returned to normal.

CS_2 was detected in the urine of children in a study of persons living near a Czechoslovakian industrial plant emitting 32 kg/h H_2S and

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*Magos, L., et al. (1974). "Half-Life of CS_2 in Rats in Relation to Its Effect on Brain Catecholamines," Int. Arch. Arbeitsmed., Vol. 32, p. 289.

†Vasileva, I. A. (1973), "Effect of Small Concentrations of CS_2 and H_2S on the Menstrual Function of Women and the Estryl Cycle of Experimental Animals," Gigiena i Sanitaria, Vol. 7, p. 24 (transl. from Russian).

‡Lancranjan, I. (1972), "Alteration of Spermatic Liquid in Patients Chronically Poisoned by Carbon Disulphide," Med. Lavoro, Vol. 63, No. 12, p. 29.

§Rozewichi, S., et al. (1973), "Effect of Chronic Poisoning with Carbon Disulfide on the Hormone Activities of Rat Ovaries," Med. Pr., Vol. 24, p. 133.

**Kuwai, S. (1960), "Experimental Studies on Gas Inhalation of Respective and Combined CS_2 and H_2S," Shikoku Igaku Zasshi, Vol. 16, Suppl. 144, p. 64.

and 55.5 kg/h CS_2. The incidence of upper respiratory passage disease was noted to be 10 percent higher in this industrial group than in a rural control group (Holasova, 1969).*

Threshold Levels

It is apparent that 20 ppm CS_2 allows little if any margin of safety for chronic CS_2 exposure. Current allowable concentrations for occupational exposures are 20 ppm in the United States, (ACGIH, 1971),* 3 ppm in the USSR, and 10 ppm in Czechoslovak. (Brieger and Teisinger, 1967). The 20-ppm level has received considerable critisicm; Finnish authorities reduced the level to 10 ppm in 1972 (Tolonen et al., 1975).

In estimating the allowable concentration in the ambient atmosphere from epidemiological studies of industrial exposures, one must consider that the workers are (aside from exposure effects) normal, healthy males performing manual operations, and that they are exposed less than eight hours per day for five days per week. In these groups, cardiovascular and neurological effects have been noted from chronic (intermittent) exposures approaching 10 ppm. Disruption of the estrous cycle of working women was also noted at exposures to 4 ppm. Continual exposure (i.e., 24 hours/day) does not occur for the worker (i.e., 8 hours/working day); thus reversible effects would tend to be restored on a diurnal basis until an equilibrium has been established. Using the 35 minute half-life for CS_2 in man established by Magos (1974), the chronic damage must either be irreversible or caused by a long-lived metabolite. Tolonen et al. (1975)

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*Holasova, P. (1969), "Pathology of Children in an Area Polluted with CS_2 and H_2S in Comparison with a Control Group," Cesk. Hyg., Vol. 14, p. 7; Vol. 8, p. 260.

*ACGIH (1971), "Documentation of Threshold Limit Values," 3rd edition (American Council of Governmental and Industrial Hygienists).

noted that 40 percent of his historically exposed group had not been exposed for the five-and-one-half-year period in which the elevated CHD mortality rate was significantly greater. Thus the CHD effects appear irreversible. In contrast, some studies have noted reversible occurrences at the biochemical level (i.e., mixed-function oxidase inhibition). Reversible impairments would be continuous under constant exposure and thus, in general, indistinguishable from irreversible alterations. In rats continuously exposed to levels of 100 $\mu g\ CS_2/m^3$ (0.03 ppm) the rate of body weight increase and content of coproporphyrin in urine was decreased (Misiakiewicz et al., 1971).* Baikov (1974)* found eye sensitivity to light reflexes affected at 10 $\mu g/m^3$ (3 ppb) in humans.

For continual exposure to CS_2, the morbidity threshold effect for humans is presumably lower than 10 ppm. A certain fraction of the population is predisposed to symptoms that continuous levels of CS_2 may further aggravate (e.g., hypertension, elevated cholesterol). It appears that persons on mineral-deficient diets may also be more susceptible to toxic effects (ACGIH, 1971). To establish a critical margin of safety for the general population, further research on threshold effects to critical subgroups needs to be carried out. In light of the above, an ambient standard should be developed that allows a magnitude of difference for chronic-intermittent versus chronic-continuous exposure, as well as another magnitude for critical subgroups that may be further impaired. We recommend a level equal to or less than 300 $\mu g\ CS_2/m^3$. Such a level should provide an adequate health effects margin of safety for the general population until further studies on continual exposure thresholds are performed.

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* Misiakiewicz, A., et al. (1971), "Effect on Animals of Prolonged Exposure to Low Concentration of CS_2 in the Air," Roc. Panstw. Zakl. Hig., Vol. 22, No. 1, p. 7.

* Baikov, B. K. (1974), "Hygienic Effect of Carbon Bisulfide and Hydrogen Sulfide Simultaneously Present in Atmospheric Air," microfiche, transl. from Russian, Information Systems Inc., Omaha, Nebraska.

Because of the lack of data on chronic COS health effects, a margin of safety should be established by analogy to CS_2. The basis for this analogy is the similarity in chemical and physical properties, the possible relationship in biochemical metabolism and mechanism of toxic effect (reactive sulfur atom), and the similarity in acute exposure thresholds and symptomatology. Using a ratio (CS_2/COS) of molecular weights of 1.25 and a ratio of toxicity of 2 (reactive sulfur atoms), we recommend an ambient level of 0.16 ppm COS (400 $\mu g/m^3$) until further studies are performed.

It should be noted that the maximum allowable concentration for CS_2 in the workplace in the USSR is 10 mg/m^3 (3.3 ppm) and in the ambient air 10 $\mu g/m^3$ (3.3 ppb)(Baikov, 1974). These concentrations are considered as goals rather than as regulatory ceilings and are frequently exceeded.

Welfare Effects

CS_2 has received wide application as a fumigant pesticide in the control of mosquito larvae, wax moths, nematodes, ants, fungi, and flour beetles. The concentrations employed are quite high; generally greater than 5000 ppm is required to produce the desired effect. CS_2 is controlled as a food additive for the fumigation of processed grains in the production of fermented malt beverages under the Federal Food, Drug, and Cosmetic Act (Federal Register, 1964).* Residues must be absent in the finished beverages.

CS_2 increases the efficiency of seed germination for Zea mays (corn) (Popescu et al., 1971).* Concentrations of CS_2 up to 10 percent stimulate

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*Federal Register (1964), "Fumigants for Processed Grains Used in the Production of Fermented Malt Beverages," Fed. Reg., Vol. 29, p. 7462.

*Popescu, V., et al. (1971), "Influence of the Treatment with Some Chemicals on the Seed Germination of Several Cultivated Plants," Ser. Biol., Vol. 16, p. 101.

CO_2 fixation in alfalfa leaves and higher concentrations stimulate the formation of l-alanine (Lehman et al., 1972).* Low seedling weight and reduced glucose content were observed in wheat seeds that were treated with high concentrations of CS_2 and stored for six months (Zaki and Nada, 1964).* These studies indicate that there would be little impact of CS_2 on plants at expected ambient concentrations.

Kauch (1962) found 12 ppm COS in horseradish tissue and suggests the substance as a defensive compound for plants. In a study to characterize odor-producing substances from cattle feedlots, Elliott and Travis (1973) found COS produced in significant quantities. COS is reported to have an unpleasant odor similar to that of rotten eggs; however, no threshold data are reported in the literature.

Pure COS has a foul ethereal odor, however, according to Patty (1963), it does not offer adequate warning at harmful concentrations. A solution of 1 mg CS_2/per liter of water is said to be the threshold for detection by smell (Vinogradov, 1966).‡ Balkov (1974) found an odor threshold of 0.08 mg/m^3 in air.

There are reports in the literature concerning the corrosive properties of CS_2 on metallic coatings during its manufacture; however, at emission concentrations (100 ppm) this effect would not be a problem.

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*Lehman, J., et al. (1972). "Effect of Some Vaporized Lipophilic Solvents on Carbon Dioxide Fixation by Alfalfa," Experientia, Vol. 28, No. 12, p. 1415.

*Zaki, M., and M. Nada (1964). "Effect of CS_2 on the Total Carbohydrate Content of Treated Wheat Seeds," Ann. Agr. Sci. (Cairo), Vol. 6, No. 1, p. 1350.

‡Vinogradov, P. S. (1966). "New Experimental Data for Substantiating the Maximum Permissible Concentration of Carbon Disulfide in Water Basins," Gigiena i Sanitaria, Vol. 31, p. 13.

Environmental Quality Aspects

It appears that the primary anthropogenic controllable source for CS_2 emissions is from viscose rayon manufacturing. Emissions from refinery sulfur recovery plant., assuming Beavon catalyst degradation, would contribute approximately 30 percent of the anthropogenic emissions in the Los Angeles basin. For the five-day stagnation conditions previously given for the Los Angeles Basin (Estimates of Ambient Air Concentrations), the threshold odor concentration (80 $\mu g/m^3$) would be exceeded. Contributions from other sources do not appear to be significant, and under the assumed conditions of stagnation, our 300 $\mu g/m^3$ recommended health effects threshold would not be exceeded.

Little is known about the health effects of COS. Because of its significant emission from some nonselective reducing catalyst systems, however, establishing the threshold effect is worthy of immediate consideration. Based on analogy to CS_2, a 400 $\mu g/m^3$ health effects level is recommended until more data are available. Under the worst case conditions (as above) this level will not be exceeded. The odor threshold is not known, but, if similar to CS_2, it will frequently be exceeded.

Coal gasification plants may emit significant quantities of COS and CS_2 and may pose aesthetic problems (odor) in the vicinity of the source along the plume. This will depend on the sulfur content of the coal being gasified. Oil shale retorting and upgrading plants will also emit significant quantities of CS_2 and COS, and likewise may pose aesthetic problems in the near vicinity. In these plants, however, annual time-weighted ambient air concentrations above 300 $\mu g\ CS_2/m^3$ and 400 $\mu g\ COS/m^3$ should not be exceeded.

Due to the generally long environmental half-lives for each compound, the transformations to H_2S and SO_2 would occur, but after appreciable dilution of the vapors in the atmosphere.

IV REFERENCES

ACGIH (1971), "Documentation of Threshold Limit Values," 3rd edition (American Council of Government and Industrial Hygienists).

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